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# Glycine at the Pyrite–Water Interface: An *ab initio* Metadynamics Study

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This research focuses on a prebiotic synthesis scenario of peptides at extreme conditions similar to those near hydrothermal vents. It aims to assess the importance of such high temperature and pressure conditions including mineral surfaces and to gain vital molecular level understanding about these reactions, which is otherwise not possible to obtain in laboratory experiments. The work presented here is about large–scale *ab initio* Car–Parrinello molecular dynamics simulations on characterizing the reactivity of the ideal and the defective pyrite surface having an interface with water at 500 K and about 20 MPa. Desorption mechanisms and free energies for desorption are obtained from *ab initio* metadynamics simulations. Surface defects are found to have an important role in stabilizing the reactant molecules on the surface.

## 1 Introduction

The quest for a molecular level understanding of chemical reactions and the role of prebiotic conditions in the formation of macromolecules of contemporary biology from small organic molecules is at the heart of our research endeavour. Among the vastly different hypotheses put forward on how life originated on earth, the one suggested by Wächtershäuser[1–3] named 'Iron Sulfur World' (ISW) hypothesis, is under great attention, especially due to exceptionally specific details at the molecular level. Wächtershäuser envisages a chemoautotrophic origin of life and the basic reactions are believed to have taken place near undersea hydrothermal vents. Successful carbon–insertion reactions[4–6] and synthesis of peptides[7,8] in laboratory experiments mimicking hydrothermal conditions brought a strong support to this hypothesis recently[9].

An interesting idea has been suggested for the activation of amino acids that makes use of an inorganic compound called carbonyl sulfide (COS), an effluent gas from hydrothermal vents; alternatively it can be generated from CO and $H_2S$ in the presence of suitable minerals[7]. Though a very small yield of peptides are found in laboratory experiments at elevated temperature, the detailed mechanism or the energetics of these reaction sequences are not known. The mechanistic insights into the formation of NCA from amino acids and COS are limited to the early speculations in footnote (16) of Ref.[10] and some evidence for the presence of an isocyanate species[8].

One reason for the lack of in–depth understanding[11] of these reactions is that the controlled reaction studies in experiments at water/mineral interfaces subject to extreme conditions are extremely challenging. In contrast, conditions which may be hard or even impossible to meet in the laboratory might be accessible 'in silico'. Computational approaches have the benefit that the reactions can be very well controlled and analyzed, in particular the influence of different reaction conditions, for e.g. extreme versus ambient, can be substantiated while keeping all other parameters unchanged. Different chemical reaction pathways can be traced and mechanism as well as free energy barriers involved

can be examined at the molecular level in computer simulations. Recent advances in *ab initio* molecular dynamics[12,13] together with the modern computer infrastructure, like the IBM Blue Gene/L machine 'JUBL' at John von Neumann Institute for Computing at Forschungszentrum Jülich, make it possible to study such complex chemical reactions fully 'in silico'.

In this work we set our aim to look at the reactivity of a wet mineral surface at extreme thermodynamic conditions in our 'virtual lab' approach. In the ISW scenario, it is important that the metabolites stay at the pyrite surface until they concentrate, react and/or undergo structural changes. Thus in the first *ab initio* molecular dynamics simulation at 'ISW conditions' carried out in our laboratory[14] we focused on glycine adsorption at the pyrite–water interface using an ideal (001) surface of $FeS_2$ (pyrite). It was concluded that water–mediated detachment of glycine occurs on a time scale of picoseconds[14], which is much too fast to allow for chemical reactions to occur there. Starting with a bi–dentate adsorption mode with respect to the carboxylate oxygen atoms of the glycine, Pollet et al.[15] found only partial detachments, but not full desorption within 10 ps time scale. On the other hand, naturally occurring pyrite has plenty of surface defects, predominantly missing sulfur atoms. We have recently shown that such defects increase the reactivity and time scale for desorption[16]. Most importantly, these works underlined the role of hydrogen bonding of the aqueous environment in the desorption processes.

In the presented work, we will look at full desorption of the bidentate adsorption mode considered by Pollet et al.[15]. The detailed desorption mechanism and the associated free energy landscape and barriers are computed employing the *ab initio* metadynamics technique. The results are compared with the desorption at the defective pyrite surface having a single sulfur vacancy[16].

## 2 System Setup

The mineral surface was modelled by a pyrite ($FeS_2$) slab consisting of 24 Fe and 48 S atoms. We used an orthorhombic periodic box of dimensions $10.8 \times 10.8 \times 18.9$ Å[14–16]. The supercell contained 36 water molecules corresponding to a density of $\approx 0.85$ g/cm$^3$[17] between two layers of pyrite; see Fig. 1. The pyrite slab exposed the (001) surface towards water mimicking a water/pyrite interface in terms of a standard slab setup. The whole system was thermostated to 500 K resulting in an expected pressure of about 20 MPa and the surface vacancy was created by removing one of the threefold coordinated surface sulfur atoms.

## 3 *Ab initio* Molecular Dynamics and Metadynamics

*Ab initio* molecular dynamics[12,13] is well suited for the present project where all calculations were performed within spin–restricted Kohn–Sham density functional theory in its plane wave / pseudopotential formulation[13]. Details are skipped here but are presented in Ref.[15,16,22]. Our previous calculations demonstrated that using this setup the unit cell parameters[15] and the electronic structure[16] are reproduced very well. All calculations presented here were performed with the `CPMD` simulation package[18,13].

Most of the chemical reactions of our concern occur at time scales which are several orders of magnitude beyond those accessible by standard *ab initio* molecular dynamics.

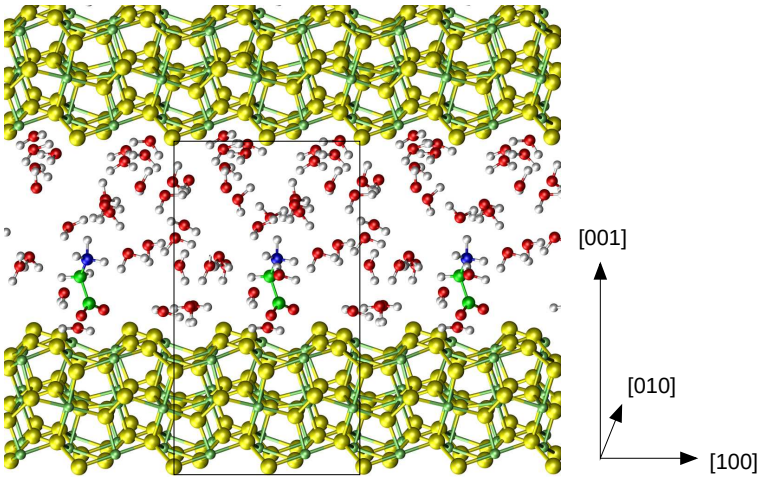


Figure 1. Supercell (black box) used for the simulations of glycine adsorbed at the (001) surface of pyrite in contact with hot–pressurized water; periodic images are included in the [100] and [001] directions to guide the eye. Color code: hydrogen (white), oxygen (red), carbon (green), nitrogen (blue), sulfur (yellow), iron (light green).

For overcoming the timescale limitation by accelerating the sampling of rare events and to estimate free energies and barriers we used the metadynamics technique[19] in its extended Lagrangian formulation[20], see Ref.[21] for a review. At the heart of this technique is a coarse–graining approach where selected degrees of freedom are represented by a small set of collective coordinates[19]. Within this subspace the free energy hypersurface spanned by the collective coordinates is sampled by placing auxiliary Gaussian potentials along the dynamical time evolution. This biasing potential is slowly grown during the 'metadynamics' of the collective coordinates and finally the system is forced to escape from the initial free energy minimum thus exploring reaction pathways. As the added biasing potential compensates the underlying free energy surface the method allows one to map the free energy surface by reconstructing the sum of the added Gaussians. One of the great advantages of this approach is that it enables one to explore not–foreseen transformation and reaction pathways[21].

## 4 Results

### 4.1 Desorption of Glycine from the Ideal Surface

In the following we present the desorption study of the bidentate adsorption mode of zwitterionic glycine as sketched in structure **1** of Fig. 2. In earlier investigations of Pollet et al.[15] using short–timescale *ab initio* molecular dynamics it was found that the carboxylate oxygen atoms were partially detaching several times due to hydrogen bonding interactions with water. This behaviour is in stark contrast to that observed in the previous study[14] where a monodentate zwitterionic glycine on the ideal pyrite surface desorbs readily within 1.5 ps. In order to assess the stability of the bidentate adsorption mode in terms of free energy

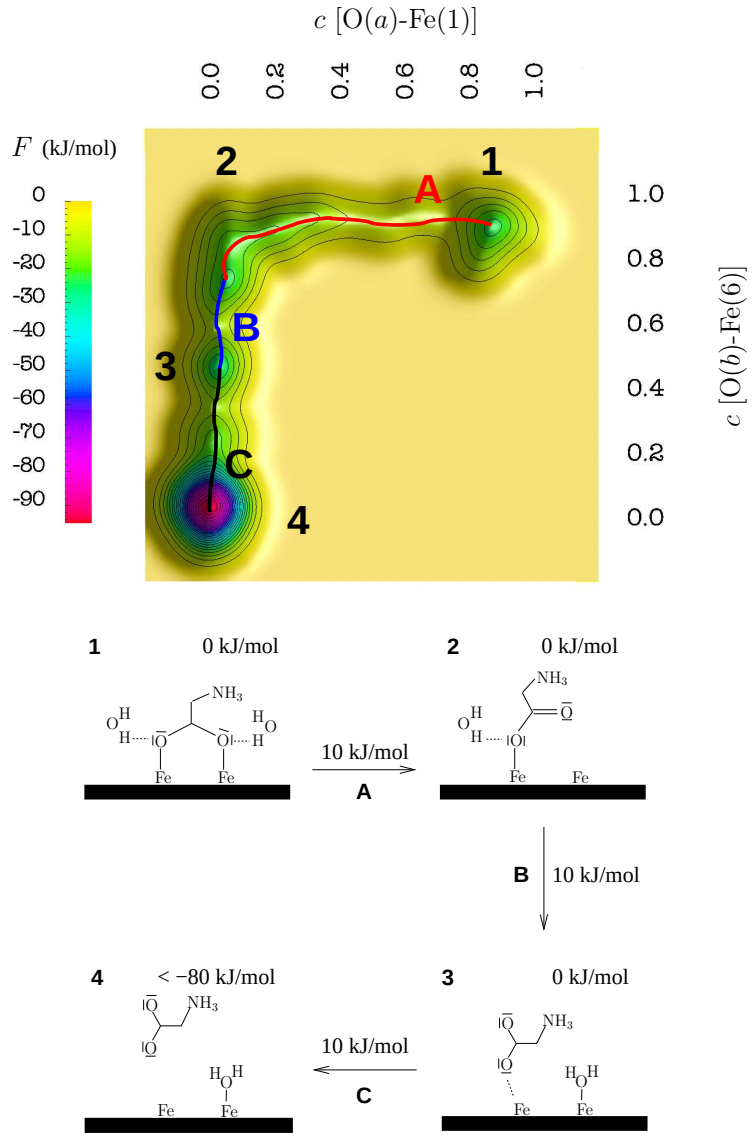


Figure 2. Free energy surface (top) represented in collective coordinate space and corresponding schematic mechanism (bottom) for the desorption process of glycine in the bidentate zwitterionic adsorption mode **1** at the $FeS_2$(001)–water interface under ISW conditions. Bold numbers and letters denote free energy minima and minimum free energy paths connecting the wells, respectively. The energies in units of kJ/mol associated with structures are the free energies relative to the initial structure **1** and those associated with arrows are free energy barriers.

landscapes and retention times and to investigate the underlying desorption mechanism in pertinent detail we employed *ab initio* metadynamics to enforce the desorption process.

The starting structure **1** of our simulation was the final structure of the simulation by

Pollet et al.[15], i. e. a structure after 10 ps of standard *ab initio* simulations. In the starting structure **1** two carboxylate oxygen atoms are connected to the surface iron atoms and hydrogen bonds exist between water molecules and the carboxylate oxygens. The free energy surface obtained from the metadynamics simulation together with the schematic mechanism along the minimum *free* energy path are given in Fig. 2. Detachment of first carboxylate oxygen occurs forming a monodentate structure **2** by overcoming a free energy barrier of about 10 kJ/mol. Subsequently the O–Fe bond of **2** breaks to form structure **3** which is a partially dissociated structure, held near the surface by the hydrogen bond network of water. The barrier is nearly 10 kJ/mol for the conversion of **2** $\rightarrow$ **3**. For a complete desorption from structure **3** the barrier to surmount is only about 10 kJ/mol. The structures **2** and **3** have almost the same stability as the starting structure within the error bar estimate. The desorbed structure is much lower in free energy compare to all other structures. These results show that the effective barrier for the desorption of bidentate zwitterionic glycine from the ideal surface is only about 10 kJ/mol. In terms of retention time of glycine this means only a few picoseconds, which is again not sufficient for chemical reactions to occur.

### 4.2 Desorption of Glycine from Defective Surface

In order to design a more realistic mineral surface we have removed one three–fold coordinated surface sulfur atom, which mimics the presence of ubiquitous sulfur vacancies on the pyrite surface. Such defects were found to increase the reactivity compared to an ideal surface, which was probed by both electronic structure calculations and a water adsorption study around the defect site[16]. We have performed a systematic study of various adsorption modes of glycine and extracted two most likely configurations at the pyrite–water interface. The results of a cyclic adsorption mode **5** are presented in Fig. 3.

In particular, different minima and pathways were explored; see Fig. 3. Although the free energy is much lower in the fully solvated (desorbed) state of the glycine molecule, the free energy barriers allowing for desorption are quite high. Compared to the zwitterionic adsorption structure on the ideal surface, the activation barrier for the desorption of the cyclic configuration is close to an order of magnitude higher, 90 kJ/mol. This difference in the activation barriers can be traced back to the fact that the desorption of the zwitterionic form is mediated by hydrogen bonding of solvation water with the carboxylate oxygen, which is not possible for the cyclic adsorption structure due to geometric shielding effects. These results indicate that the cyclic adsorption structure, which can only be formed in the presence of surface vacancies, is stable toward desorption on a millisecond scale at the defective pyrite–water interface. The retention time of the zwitterionic configuration is extended from picoseconds on the ideal pyrite–water interface to nanoseconds in the presence of these point defects.

### 4.3 Peptide Synthesis

In parallel, we have worked out possible reaction pathways that lead from individual amino acids to peptides and established the role of ISW conditions on these chemical reactions[22]. At the heart of this work is the study of the formation a peptide bond between two glycine molecules using *ab initio* metadynamics techniques. This involved about 27 reaction steps and comprises simulations at three vastly different reaction conditions: ambient bulk water

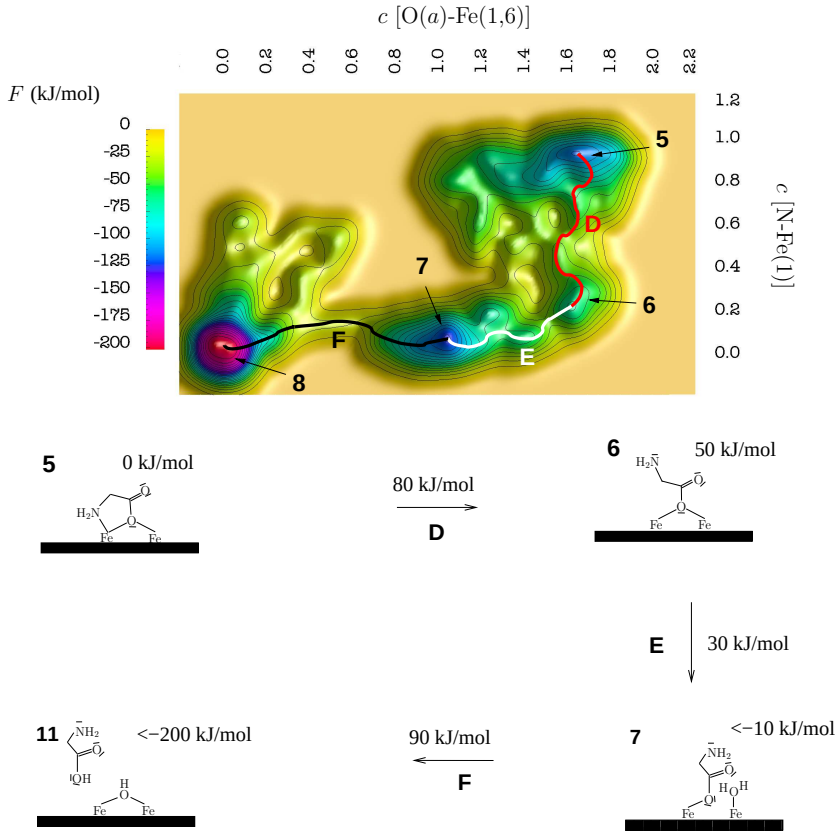


Figure 3. Free energy surface (top) represented in collective coordinate space and corresponding schematic mechanism (bottom) for the desorption process of glycine in the cyclic adsorption mode **5** at the defective $FeS_2(001)$–water interface under ISW conditions. Bold numbers and letters denote free energy minima and minimum free energy paths connecting the wells, respectively. The energies in units of kJ/mol associated with structures are free energies relative to the initial structure **5** and those associated with arrows are free energy barriers.

at about 300 K and 0.1 MPa, hot–pressurized bulk water at about 500 K and 20 MPa, and hot–pressurized water at the pyrite–water interface. These results are already presented in detail in Ref.[22] and are not discussed here.

## 5 Conclusions

Using extensive *ab initio* metadynamics simulations we have obtained mechanisms and free energy for the desorption of glycine from a hot–pressurized water interface with an ideal and a defective pyrite surface. We have shown that surface defects are necessary for retaining glycine on the surface for long enough times to allow for chemical reactions to occur, which is an essential prerequisite for heterogenous catalysis of prebiotic reactions at mineral surfaces. Access to a supercomputing infrastructure like the IBM Blue Gene/L machine at NIC enabled us to investigate vital primordial chemical reactions and to estimate

their associated free energies employing large scale *ab initio* simulations.

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